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# Enhancement of Perfluoropolyether Boundary Lubrication Performance

## I. Preliminary Results

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## Summary

A ball bearing simulator operating under starved conditions was used to evaluate the boundary lubrication performance of a perfluoropolyether (PFPE), Krytox 143 AB. Several approaches to enhance boundary lubrication were studied. These included: (1) soluble boundary additives, (2) bearing surface modifications, (3) "run-in" surface films and (4) ceramic bearing components. In addition, results were compared with two non-perfluorinated liquid lubricant formulations. Based on these preliminary tests, the following tentative conclusions can be made: (1) Substantial improvements in boundary lubrication performance were observed with a  $\beta$ -diketone boundary additive and a tricresyl phosphate (TCP) liquid surface pretreatment, (2) the use of rough  $\text{Si}_3\text{N}_4$  balls ( $R_a = 40 \mu\text{in}$ ) also provided substantial improvement but with concomitant abrasive wear, (3) marginal improvements were seen with two boundary additives (a phosphine and a phosphatriazine) and a neat (100 percent) fluid (a carboxylic acid terminated PFPE); and surface pretreatments with synthetic hydrocarbons, a PTFE coating, and TiC coated 440C and smooth  $\text{Si}_3\text{N}_4$  balls ( $R_a < 1 \mu\text{in}$ ), and (4) two non-PFPE lubricant formulations (a PAO and a synthetic hydrocarbon) yielded substantial improvements.

## Introduction

Perfluoropolyethers (PFPE) have been used as lubricants for a variety of spacecraft applications for more than two decades

(refs. 1 and 2). In addition, these fluids are candidates for high temperature aeronautical applications (ref. 3). Several commercial fluids are available, such as Krytox (ref. 4), Fomblin Z and Y (refs. 5 and 6), and Demnum (ref. 7). Of these fluids, only Krytox and Fomblin Z have been used extensively as liquid lubricants and greases for space applications (ref. 8).

Conventional lubricants are always supplied with an additive package that enhances their performance. These additives include: antiwear, EP, anti-oxidant, anti-degradation, anti-corrosion, etc. In contrast, PFPE's are usually supplied as unformulated (nonadditive) basestocks. This is because conventional additives developed for mineral oils, esters, hydrocarbons, etc. are not soluble in PFPE fluids.

A few PFPE soluble additives have been developed. The first synthesized additives were to function as degradation inhibitors at high temperatures. These included phosphines (ref. 9 to 11) and phosphatriazines (refs. 12 to 14). The perfluoroaryl phosphines have been reported to extend the upper temperature limits of Krytox fluids to  $343^\circ\text{C}$  and Fomblin Z fluids to  $288^\circ\text{C}$  (ref. 15). However, other data (ref. 16) have shown the loss of additive function at  $343^\circ\text{C}$ . There is also limited activity for both additive types at  $316^\circ\text{C}$  (ref. 12) and limited time of activity (75 to 100 hr) at  $288^\circ\text{C}$  (ref. 13). X-Ray photoelectron spectroscopy (XPS) studies (ref. 17) of the passivation film formed on M-50 steel surfaces during oxidation-corrosion testing with a PFPE fluid containing a perfluoroaryl phosphine concluded that protective action was afforded by high surface concentrations of some type of phosphorus compound.

Basset and Hermant (ref. 18) reported antiwear activity for a series of fluorinated carboxylic acids and their amine salts. However, only a hydrocarbon basestock was studied. It was concluded that the acids formed a soap that was subsequently converted into surface fluoride. Masuko et al (ref. 19) studied a series of PFPE derivatives (acids, alcohols, and phosphate esters) in a Demnum basestock using a vacuum four-ball apparatus. These additives yielded antiwear activity with the PFPE acid being the most effective. Sharma et al (ref. 20) reported antiwear activity for an additive (structure not disclosed) in Fomblin Z.

Later, this was reported (ref. 21) to be an alcohol terminated PFPE. Reference 21 also reported wear reduction for a PFPE ketone. Recently, four-ball wear results (ref. 22) have been reported for two other PFPE derivatives: a polar amine salt and a phosphorus containing end group. These additives yielded promising results in Fomblin Z and Fomblin Y base fluids to 200 °C. A different class of additives (halogenated aryl esters) has been successfully developed for the lubrication of gold coated slip rings (ref. 23).

A unique bearing simulator (ref. 24) has been developed for the evaluation of lubricant formulations and surface treatments. This device, known as the WAM 3 apparatus, can also generate a complete performance map showing the transitions from boundary to mixed and finally to EHL lubrication.

Therefore, the objective of this work was to use this apparatus to develop a test protocol in order to determine the enhancement of the boundary lubricating ability of a PFPE (Krytox 143AB) by the use of (1) soluble boundary additives, (2) bearing surface modifications, (3) run-in surface films, and (4) ceramic bearing components. In addition, results are compared with two non-perfluorinated liquid lubricant formulations.

## Experimental

### Test Fluids

Three different liquid lubricants were used in this study: (1) an unformulated perfluoropolyether (Krytox 143AB), (2) a formulated synthetic hydrocarbon (Nye 2001), and (3) a formulated polyalphaolefin (Nye 176A). Typical properties and additive contents appear in table I.

### Lubricant Additives

Three lubricant additives (at one weight percent) were evaluated in the PFPE basestock: (1) a phenyl phosphine, (2) a mono-phosphatriazine, and (3) a PFPE  $\beta$ -diketone. In addition, a fourth material (commercially available), a carboxylic acid terminated PFPE, was studied neat (100 percent). Additive structures and designations appear in table II.

### Simulator

The simulator is fully described in reference 24. Test configuration consists of a ball-on-disc, as shown in figure 1. Balls (20.64 or 12.7 mm dia) and discs (10.2 cm dia and 12.7 mm thick) were made of 440C stainless steel. These specimens can be operated over a large range of loads, rolling and sliding velocities, temperatures and environmental conditions. Both ball and disk surface speeds and directions can be controlled. Therefore, a large range of rolling (R) and sliding (S) velocities can be introduced. Independent control of R and S provide a "decoupling" of the entraining velocity in the inlet region from the sliding velocity in the Hertzian region. This provides a method of separating the interaction between the physical and chemical properties of the lubricant.

### Procedure

A marginal (starved) lubrication scheme was used. Specimens were first ultrasonically cleaned in petroleum ether for 5 min, followed by an additional 5 min in acetone. The ball and disc specimens were then wet with 0.5 ml of test lubricant, spun at 2000 rpm (ball) and 1350 rpm (disc) for two minutes prior to testing. Only a thin film (reproducible amount) of lubricant remains on the specimens. Tests are conducted at a normal contact pressure of 1.38 GPa (200 Ksi), a rolling velocity of 1.27 m/sec. and at room temperature (23 °C) in an air environment. The lubricant thickness between the ball and disc is decreased further during testing by introduction of contact slip. Per cent slip is defined as:

$$\% \text{ Slip} = S/R \times 100 \quad (1)$$

where

$$R = \text{Rolling Velocity} = 1/2 (V_d + V_b) \quad (2)$$

$$S = \text{Sliding Velocity} = V_d - V_b \quad (3)$$

where

$$V_d = \text{disc velocity at contact}$$

$$V_b = \text{ball velocity at contact}$$

The first 300 sec., after loading, is operated under pure rolling. At 300 sec. and every subsequent 100 sec., contact slip is increased by 2 percent until 10 percent slip is attained at 700 sec. At 900 sec. and every subsequent 200 sec., slip is increased by 5 percent until 1900 sec., when a slip of 40 percent is attained. This contact slip is maintained to the end of test at 2400 sec. This procedure (designated as "A") was used for all tests using the 12.7 mm dia ball specimens.

Some preliminary tests were conducted with larger balls (20.64 mm dia) and a different test protocol ("B"). Specimens were wetted with 0.5 ml of lubricant and spun at 2000 rpm (ball) and 1200 rpm (disc) for two minutes. As in procedure "A", the first 300 sec. were run under pure rolling. At 300 sec and every 100 sec, the contact slip is increased by 2 percent until 10 percent at 700 sec. At 900 sec, slip is increased to 15 percent and to 20 percent at 1500 sec. Twenty percent slip is maintained until test termination at 1800 sec. These tests were run at a rolling velocity of 2.54 m/sec.

All tests were continued until there was a rapid increase in traction coefficient which signified contact failure. When no failure occurred, tests were suspended at 1800 sec. (for the preliminary test "B") and 2400 sec (standard test "A"). A post-test analysis of the contact regions on both specimens was performed by optical microscopy.

## Results

### Preliminary Screening

The Krytox 143 AB base fluid, two additive formulations (1 wt %) and the neat (100 percent) PFPE carboxylic acid were evaluated using test protocol "B". The additives are designated as TL-1, TL-2 and the carboxylic acid as 157 FSL. These represent the phenylphosphine, mono-phosphatriazine, and PFPE carboxylic acid, respectively (table II). Typical traction coefficient as a function of time traces appear in figures 2(a) to (d), respectively.

For the Krytox base fluid, figure 2(a), under pure rolling conditions, the traction coefficient is very low. As the first slip step (2 percent) is introduced, the traction rises quickly to about 0.15 and remains level until at a 6 percent slip level, the contact fails and traction rapidly increases and the test is terminated at about 600 sec. In contrast, the phenylphosphine formulation, figure 2(b), completed the full 1800 second test with a final traction coefficient of about 0.10. The phosphatriazine, figure 2(c), and the neat carboxylic acid, figure 2(d), yielded almost identical results. The final traction value for the acid was lower, 0.08. All tests (test duration) are summarized in figure 3.

As shown in figure 3, marginal improvements (increase in average test duration) were observed for the two additive formulations and the neat (100 percent) PFPE acid, compared to the unformulated base stock. It is obvious that there is a wide variance in the data. One test with the base stock was suspended (no failure), while some of the formulations failed at low slip levels.

### Standard Tests—Alternative Lubricants

Results using the standard test protocol "A" for the two alternative lubricant formulations (Nye 2001 and Nye 176A)

and the  $\beta$ -diketone additive in 143 AB appear in figure 4. Baseline data for 143 AB is shown for comparison. As can be seen, the Krytox base fluid failed in less than 600 seconds at 6 percent slip. In contrast, the two hydrocarbon based formulations yielded substantial improvements. In addition, the  $\beta$ -diketone PFPE formulation showed substantially longer test durations.

### Standard Tests—"Run-In" Films

Tricresyl phosphate (TCP), in both liquid and vapor form, were used to generate "run-in" surface films prior to tests with 143 AB. Only two tests were performed and appear in figure 5. Both TCP vapor and liquid completed the 2400 sec test without failure. The specimens were solvent cleaned and relubricated with 143 AB using the standard protocol. The "run-in" film produced with TCP vapor allowed the Krytox to survive to about 700 sec and 10 percent slip. In contrast, the TCP liquid film allowed the Krytox to complete the 2400 sec test.

### Standard Tests—Other Surface Pretreatments

Results using other surface pretreatments using hydrocarbon lubricant formulations (Nye 176A, Nye 2001, and Mobil SHC) and a burnished Vydax (PTFE) film, appear in figure 6. Here there was no improvement with Nye 176A and only marginal improvements with the Mobil SHC, Nye 2001, and the Vydax film.

### Standard Tests—Ceramic Balls

Figure 7 contains results using hybrid systems (TiC coated 440C and  $\text{Si}_3\text{N}_4$  balls). No improvement was seen with the smooth silicon nitride ball, marginal improvement with TiC and substantial improvement with rough silicon nitride. However, the latter was accompanied by severe abrasive wear which would preclude its use in a real system.

## Discussion

Unformulated perfluoropolyethers survive in the boundary lubrication mode by decomposing into reactive species which form surface fluorides, oxides and friction polymer. These surface films, although effective in initially reducing friction and wear, usually increase the degradation rate of the lubricant. This, in turn, results in a corrosive wear phenomena that can not be sustained for long durations because of the very high wear rates produced.

Conventional lubricants (i. e. hydrocarbons, esters, etc.) also degrade in boundary contacts, but produce films that are not catalytic. In addition, almost all conventional lubricants are fortified with soluble additives which assist in

producing boundary films to provide surface protection. These additives, which are readily available, are not soluble in PFPE fluids. Methods to render them soluble usually result in loss of additive function.

There are several approaches that can be used to enhance the boundary lubrication performance of PFPE based systems. These include the use of newly synthesized PFPE soluble additives, bearing surface modifications, "run-in" surface films and the use of non-steel based bearing components.

### Lubricant Additives

The mechanism of action for PFPE boundary additives is somewhat different than additives for conventional systems. Since PFPE's are already operating in a corrosive wear mode, an additive must reduce this wear rate to an acceptable level which is determined by the life requirements of the mechanism. This can be accomplished by incorporating an additive which poisons enough catalytic sites to reduce reaction rates. An additive may also function to provide competition for the lubricant molecules by forming other compounds, such as sulfides, phosphates and carboxylic acid soaps. In addition, these surface films provide friction and wear reduction on their own.

Three of the additives in this study (the phosphine, phosphotriazine, and the carboxylic acid) are considered to be film formers. The two phosphorus compounds were actually developed for an anti-corrosion function. The fourth additive (the  $\beta$ -diketone) is considered to be a surface site blocker.  $\beta$ -diketones are well known complexing agents for polyvalent metals in their enolate form. This compound was most effective in enhancing the performance of the Krytox basestock. However, it should be pointed out that because, this was a preliminary study, the additives were only studied at an arbitrary one wt. percent level. Therefore, because of molecular weight differences (table II), the  $\beta$ -diketone was actually present at a higher molar concentration. This may have contributed to its better performance.

Masuko et al (ref. 25) reported a large reduction in steady state wear rate for a PFPE carboxylic acid (20 wt %) in vacuum using a four-ball apparatus. However, tests in air actually yielded higher wear rates than with the basestock alone.

### Surface Pretreatments

Another method of enhancing PFPE performance is to pretreat the tribological surfaces, either statically or dynamically, with a neat (100 percent) boundary additive or a formulated hydrocarbon based lubricant. Using the standard test protocol "A" with neat tricresyl phosphate (TCP) either in the form of a liquid or vapor, resulted in a successful 2400 sec test (fig. 5). When relubed with Krytox and run again, the vapor pretreatment did not improve the test results. However, the liquid pretreatment did result in a

successful test. Other pretreatments using three formulated hydrocarbons (Nye 176A, Mobil SHC and Nye 2001) and a polytetrafluoroethylene (Vydax) burnished film yielded only marginal improvements.

The theory behind the use of pretreatments is that the preformed surface films passivate the metal surface and thus reduce the corrosive wear phenomena to acceptable limits. In addition, the phosphate films formed from the additives are excellent boundary lubricants on their own. Of course, these films are eventually worn away and are not replenished. Apparently, the durability of the films formed in this study was not sufficient to show any improvements, with the possible exception of liquid TCP.

### Ceramic Components

A number of investigators (refs. 26 to 28) have proposed the use of ceramic coated or solid ceramic components to extend the life of instruments bearings for use with conventional lubricants. In addition, Carré (ref. 29) and Baxter and Hall (ref. 30) have shown life extensions for ball bearings with ceramic components using PFPE lubricants. The rationale is that the chemical interactions between the PFPE and iron can be either eliminated or reduced, thus enhancing performance. In our tests, a hybrid system was used (440C discs and either a TiC coated 440C or  $\text{Si}_3\text{N}_4$  ball). There was marginal improvement with the TiC ball but none with the smooth ( $R_a < 1 \mu\text{in}$ )  $\text{Si}_3\text{N}_4$  balls. Only the rough ( $R_a = 40 \mu\text{in}$ )  $\text{Si}_3\text{N}_4$  balls showed substantial improvement. However, these tests were accompanied by high wear of the 440C disc, at a level which was unacceptable for a real system.

### Alternative Lubricants

The two non-PFPE alternative lubricants (Nye 2001 and Nye 176A) yielded substantial improvements compared to the non-additive Krytox. Both of these lubricants contain phosphorus anti-wear additives. However, even with these conventional additive packages, only one test completed the 2400 sec protocol.

### Summary of Results

Based on preliminary tests with a PFPE (Krytox 143 AB) using a bearing simulator under starved conditions, the following results were obtained:

1. Substantial improvements in test duration were observed with a  $\beta$ -diketone boundary additive and a tricresyl phosphate (TCP) liquid surface pretreatment.
2. The substitution of rough silicon nitride balls for the 440C stainless steel balls also provided substantial improvement but with concomitant abrasive wear.
3. Marginal improvements were seen with three boundary additives (a phosphine, a phosphotriazine, and a carboxylic acid); surface pretreatments with synthetic hydrocarbons

(Mobil SHC, NYE 2001); Vydax (PTFE) coating; and TiC coated 440C and smooth silicon nitride balls.

4. Alternative lubricant formulations (non-PFPE) (Nye 176A, Nye 2001) yielded substantial improvements.

## Conclusions

1. A screening test protocol has been developed which rapidly evaluates boundary additives and surface pretreatments for PFPE based systems.

2. Substantial improvements in boundary lubrication performance of PFPE based lubricant systems can be attained through the use of selected surface pretreatments and/or soluble boundary additives.

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TABLE I.—TYPICAL PROPERTIES OF TEST LUBRICANTS

Lubricant	Description	Additive content	Viscosity at 40 °C, cS	Viscosity index	Pour point, °C	Vapor pressure, Torr at 20 °C
Krytox 143AB	Perfluoropolyether	None	230*	113	-40	$1.5 \times 10^{-6}$
NYE 2001	Synthetic Hydrocarbon	1% wt organic phosphate 1/2% wt hindered phenol	106.7	137	-55	$1.0 \times 10^{-8}$
NYE 176A	Polyalphaolefin	1% wt organic phosphate 1/2% wt hindered phenol	423	142	-43	—

\*At 20 °C.

TABLE II.—ADDITIVE STRUCTURES

Name	Designation	MW	Structure
Phenylphosphine	TL-1	1762	$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2-C_6H_5]_3P$
Phosphatriazine	TL-2	1253	$C_3F_7OCF(CF_3)CF_2O(CF_3)_2C-C \begin{array}{c} \diagup N \\ \diagdown N \end{array} P \begin{array}{c} \diagdown N \\ \diagup N \end{array} C-C(CF_3)_2OCF_2CF(CF_3)OC_3F_7$
Carboxylic acid	Krytox 15 FSL	~2500	$F \left( \begin{array}{c} CF-CF_2O \\   \\ CF_3 \end{array} \right)_n CF_2COOH$
$\beta$ -Diketone	EX-1	972	$F \left( \begin{array}{c} CFCF_2O \\   \\ CF_3 \end{array} \right)_2 C(=O)CH_2C(=O) \left( \begin{array}{c} OCF_2CF \\   \\ CF_3 \end{array} \right)_2 F$



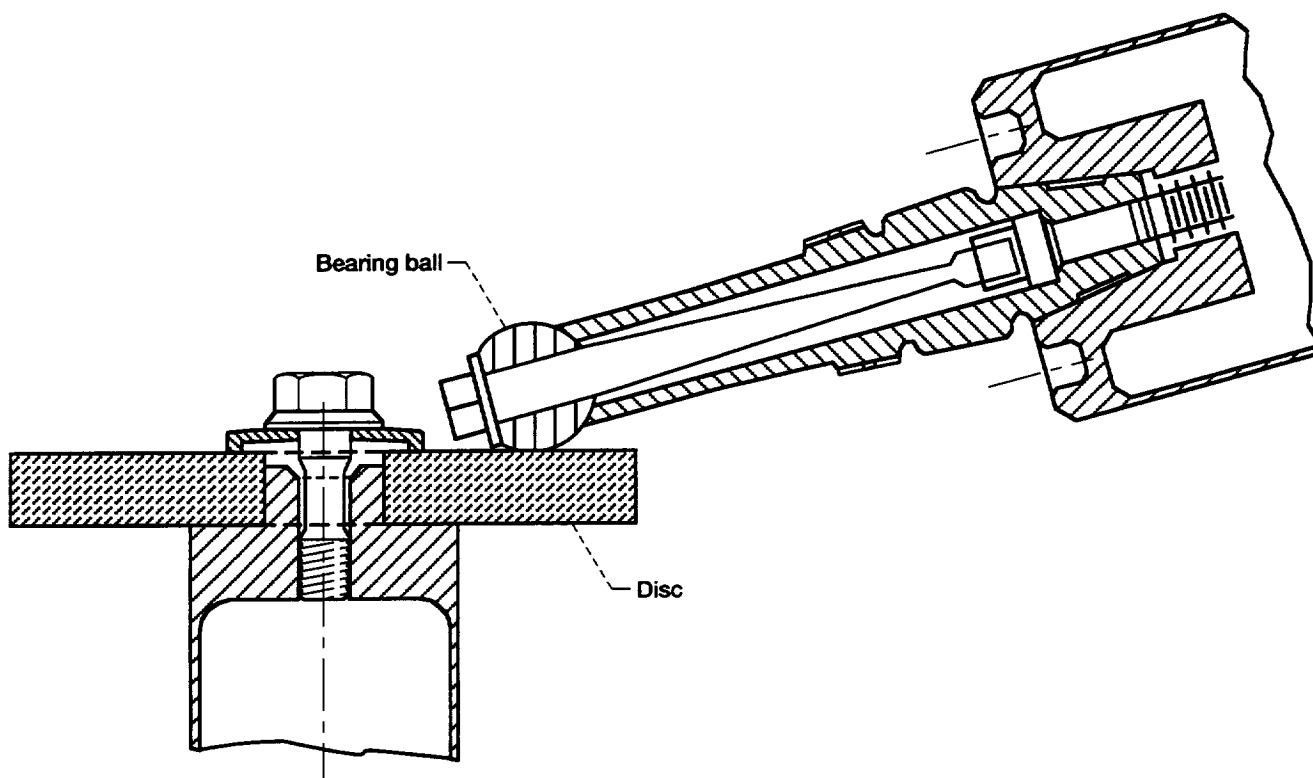


Figure 1.—Test specimen configuration.

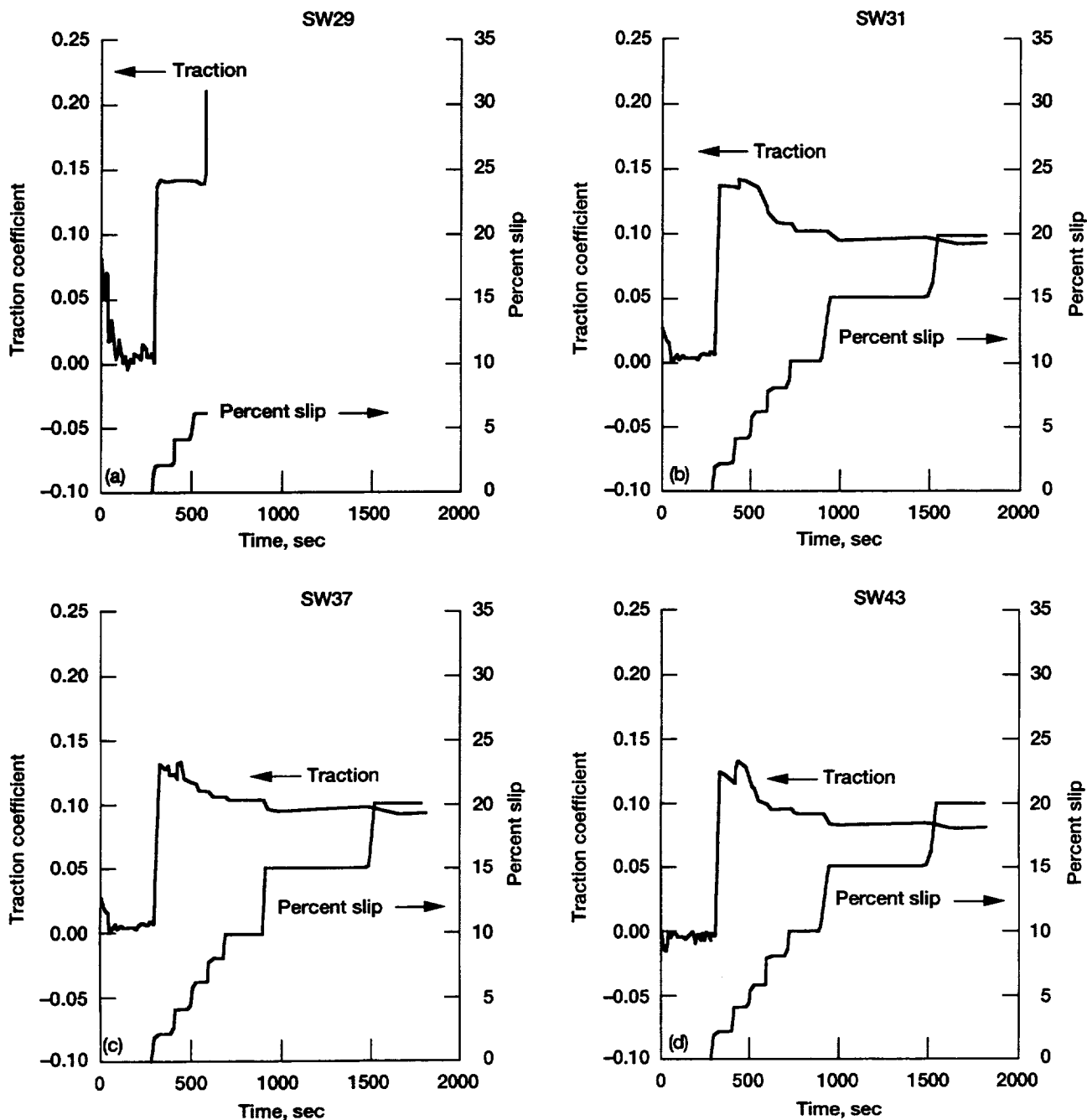


Figure 2.—Traction coefficient and slip as a function of time (test procedure "B"). (a) Krytox 143 AB base fluid. (b) Krytox 143 AB + phenylphosphine (one wt %). (c) Krytox 143 AB + phosphotriazine (one wt %). (d) Krytox 157 FSL carboxylic acid (100%).

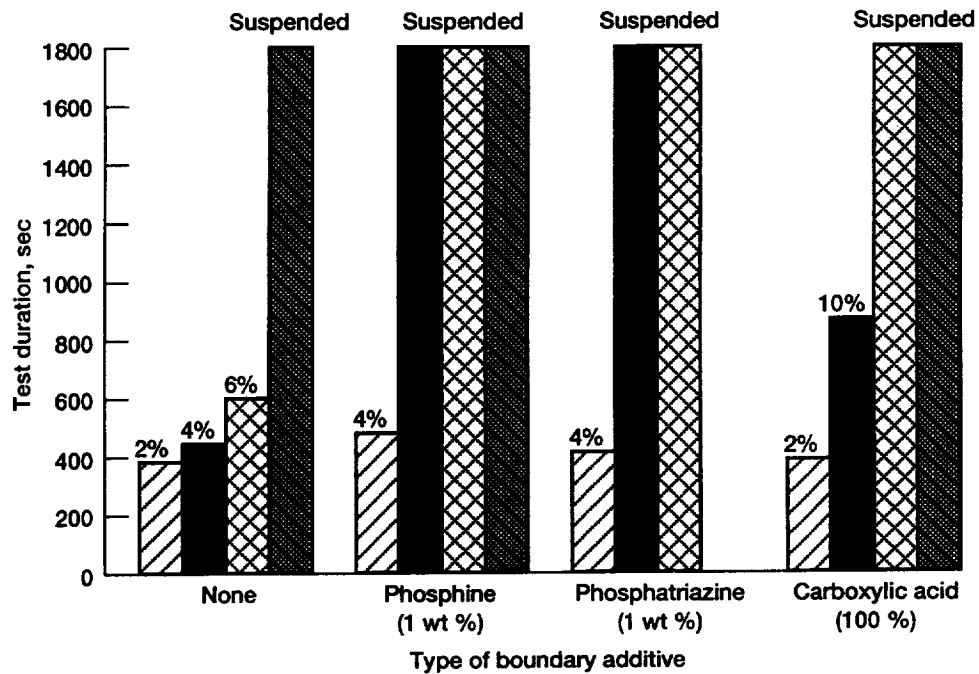


Figure 3.—Test duration for various boundary additives (Krytox 143 AB, 440C steel balls and discs) (test procedure "B").

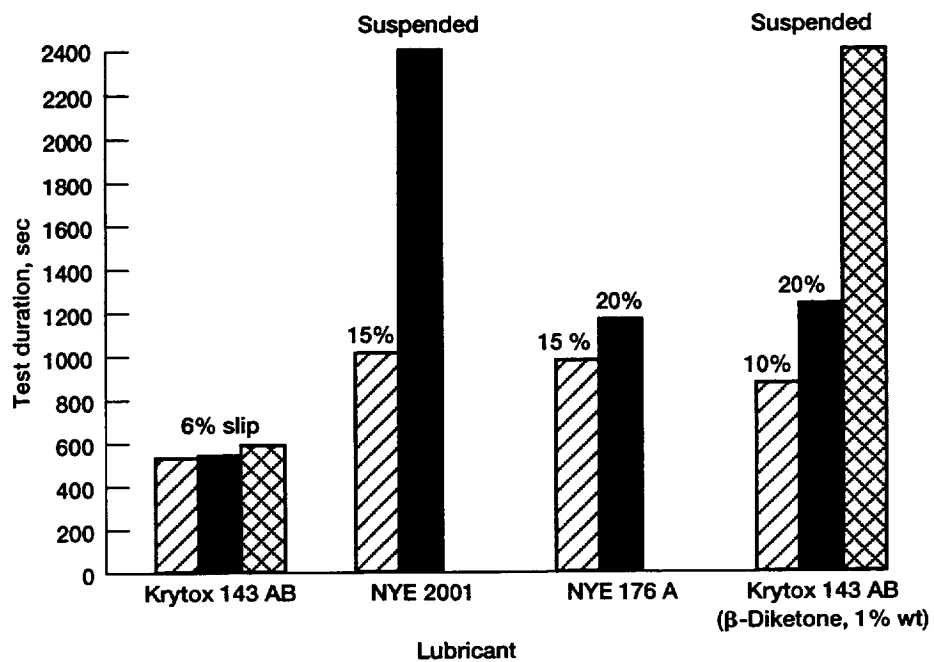


Figure 4.—Test duration for alternative lubricants (440C balls and discs) (test procedure "A").

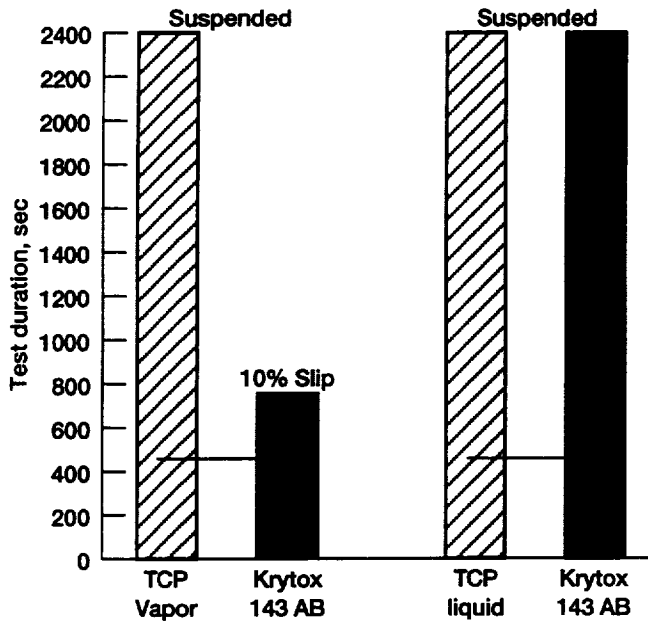


Figure 5.—Test duration for surface run-in with tricresyl phosphate (TCP) vapor and liquid (440C balls and discs) (test procedure "A").

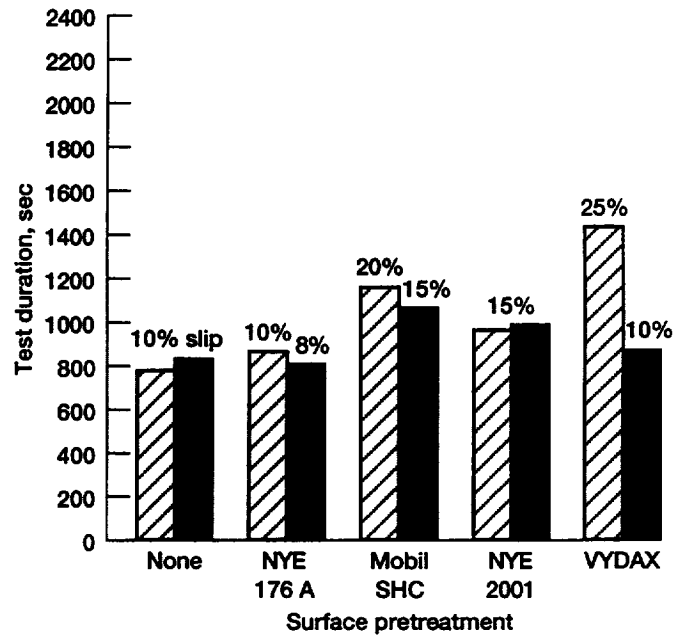


Figure 6.—Test duration for different surface pretreatments (Krytox 143 AB, 440C balls and discs) (test procedure "A").

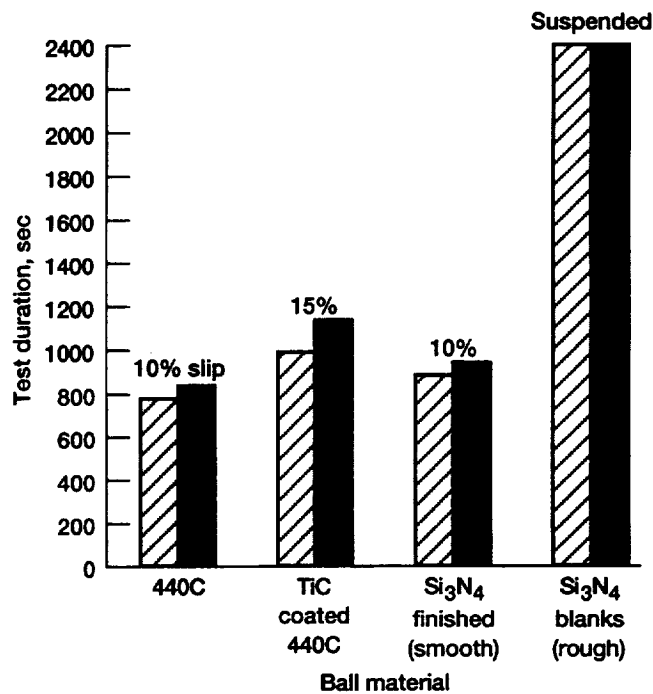


Figure 7.—Test duration for different ball materials (Krytox 143 AB, 440C discs) (test procedure "A").

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13. ABSTRACT (Maximum 200 words)  A ball bearing simulator operating under starved conditions was used to evaluate the boundary lubrication performance of a perfluoropolyether (PFPE), Krytox 143 AB. Several approaches to enhance boundary lubrication were studied. These included: (1) soluble boundary additives, (2) bearing surface modifications, (3) "run-in" surface films and (4) ceramic bearing components. In addition, results were compared with two non-perfluorinated liquid lubricant formulations. Based on these preliminary tests, the following tentative conclusions can be made: (1) Substantial improvements in boundary lubrication performance were observed with a $\beta$ -diketone boundary additive and a tricresyl phosphate (TCP) liquid surface pretreatment, (2) the use of rough $\text{Si}_3\text{N}_4$ balls ( $R_a = 40 \mu\text{in}$ ) also provided substantial improvement but with concomitant abrasive wear, (3) marginal improvements were seen with two boundary additives (a phosphine and a phosphotriazine) and a neat (100%) fluid (a carboxylic acid terminated PFPE); and surface pretreatments with synthetic hydrocarbons, a PTFE coating, and TiC coated 440C and smooth $\text{Si}_3\text{N}_4$ balls ( $R_a < 1 \mu\text{in}$ ), and (4) two non-PFPE lubricant formulations (a PAO and a synthetic hydrocarbon) yielded substantial improvements.				
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